Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-464-RC2, 2022

Comment on acp-2022-464

Anonymous Referee #2

Referee comment on "Measurement report: Changes in light absorption and molecular composition of water-soluble humic-like substances during a winter haze bloom-decay process in Guangzhou, China" by Chunlin Zou et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-464-RC2, 2022

â□□â□□This manuscript reports the measurements of the water-soluble organic carbon (WSOC) and WS-HULIS fraction of $PM_{2.5}$ samples collected in a developed region with dense populations during a haze event; the authors conducted a comprehensive analysis of the chemical composition and light absorption with their samples. They investigated the evolution of light absorption and molecular properties of these samples during one haze cycle (clean-haze bloom-haze decay-clean). While I think the subject is very interesting, there are several issues with this manuscript, including the analysis and conclusions, which are detailed below.

General comments:

- It will be necessary for the author to provide more details in the results and discussion, especially when making deductions and conclusions. This manuscript provides a very comprehensive dataset of the chemical and optical analysis of their samples. However, In the data interpretation, some of their conclusions/statements are given too simply and vaguely, which needs to be supported with more details and be more specific. For example, in explaining the variance in properties (MW, MAE, etc) of HULIS and WSOC obtained during different stages of the haze event (e.g., haze day vs clean days), the authors mostly attribute these differences to statements such as “effects of aging/oxidation/degradation” without further explanations or details. Since the aging process involves many different pathways and mechanisms, the authors will need to be more specific in the results when explaining the data other than just simply stating “aging”.
- The “HULIS fraction” used in this manuscript needs to be better described and defined since this is the major substance studied here. Adding some brief descriptions in the introduction would be necessary. HULIS was first reported as macromolecular organic

substances in atmospheric aerosol particles; and when used to refer to the light absorbing properties of the atmospheric aerosols, "HULIS" – humic-like substance, is more describing the similarities in the light absorption of the light absorbing organic carbons (e.g., brown carbon) with humic substances, which is a light absorption that sharply decreases from UV to visible wavelength. Also, many different methods for the extraction/isolation of HULIS have been reported, and the potential effects of the extraction/isolation procedure on the chemical/physical nature of HULIS have aroused concerns as well. For instance, the HULIS part could be large molecules formed by intermolecular force (aggregates) and the procedure (extraction solvent, PH adjustment, SPE, etc.) would largely change it. I think a discussion of the nature of HULIS and a brief explanation of your choice for the isolation method, at least under the circumstances of this manuscript, is important for the data interpretation later in the result section.

- In order to highlight the novelty of this manuscript, it's better to have a brief summary of the work about HULIS fractions/WSOC of $PM_{2.5}$ in the Pearl River Delta with emphasis on the major contributions of this manuscript to the current state of knowledge regarding this topic. I do notice there is one sentence mentioning that there are previous works regarding this topic(line 83-86), however, I think brief descriptions of the referred studies are necessary. Also, is this the only work studying the chemical/optical evolution of WSOC/HULIS/Brown carbon collected in PRD? If not, what have the other studies done?

Specific comments:

Line 37: comment for writing — "stronger" than what?

Line 44: "natural environment" It is better to be more specific here about what environment (e.g., natural aquatic / soil environment).

Line 45-46: "> 70% of light absorption in water-soluble brown carbon (BrC)" This need to be more specific about the wavelength/wavelength range or what parameters they used to compare (e.g., mass absorption coefficients, etc), if possible.

Line 114: "Field blank samples were collected without power on." Does this mean that the blank filter is "conditioned" in the air sample holder rather than conditioned in the sampling environment (e.g., passing particle-free air through the filter)? If so, can you explain why you chose this way as "blank control"?

Line 121-122: "Briefly, portions of the $PM_{2.5}$ samples (100 cm^2) were ultrasonically extracted with 50 mL of ultrapure water for 30 min. The extracts were filtered through a 0.22-μm PTFE syringe filter and then adjusted to pH of 2 with HCl…". I didn't find the description of the WSOC fraction here. Or is the extraction of WSOC the same as described for HULIS except for the PH adjustment and following procedure? I think this needs to be clarified here.

Line 232-233 “This difference may be related to the higher enrichment of light-absorbing organic species in HULIS.” The statement is oversimplified and needs more specific explanation and evidence to describe why the enrichment of light-absorbing OC doesn’t simply enhance the light absorption at certain wavelengths but the wavelength dependence (AAE).

Line 263-265: it might need to be more specific about the “secondary oxidation reaction” and “photolytic aging” here. It is "prolonged" or "enhanced" oxidation during haze? for example, the increased ozone levels associated with high levels of $PM_{2.5}$ could be a drive for oxidation during haze days.

Line 315-318: The author needs to mention that the samples used in Dasari and Wong’s work are from different sources (mostly biomass burning aerosols) and are different from the samples used in this manuscript. In addition, the method for molecular weight estimation used in Wong’s paper is also very different from this method (size-exclusion chromatography), in which the MW is estimated by the SEC column retention time, and it’s also highly dependent on the column, the mobile phase, and the sample itself (e.g., polarity, aggregation, etc). Also, line 317-318 is a bit self-contradictory: HULIS in haze undergo stronger oxidation, which usually leads to fast degradation. However, "a longer aging process" means higher stability (longer lifetime), which means the HULIS is more stable during haze days. Or, is the “longer aging” simply implying that because they have a higher MW, they will have a longer lifetime in the atmosphere? There needs some clarification.

Even if the author wanted to use these two references to support their inference about the higher stability of HULIS in this manuscript, they didn’t try to explain the variance in HULIS MW from different stages of the haze event (haze days vs clean days).

Line 324-325: “These differences can be attributed to bleaching or degradation of aromatic compounds.” As I understand it, “degradation” is one pathway that leads to bleaching, i.e., the degradation/oxidation of aromatic compounds could result in the bleaching of HULIS. There might need some clarification or rephrasing.

Line 573-574: It is unclear if the “longer aging process” here means “a longer lifetime." Is this an inference or an observation?